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Theoretical model for the electrospinning nanoporous materials process

Lan Xu [a,*], Fujuan Liu [a], Naeem Faraz [b]

[a] *National Engineering Laboratory of Modern Silk, Soochow University, Suzhou 215123, China*
[b] *Modern Textile Institute, Donghua University, Shanghai 200051, China*

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ABSTRACT

This paper deals with modeling the electrospinning nanoporous materials process. The presented theoretical models offer an in-depth insight into the physical understanding of many complex phenomena and might be very useful at shedding light on the contributing factors. Many basic properties and some special properties (such as the numbers and sizes of the pores) are tunable by adjusting electrospinning parameters such as voltage, flow rate, and others. With the increase of voltage and the decrease of flow rate, ever-increasing numbers and ever-decreasing sizes of the nanoporous microspheres have appeared. Electrospun nanoporous materials which can be regarded as thousands of Helmholtz Resonators forming together will become a kind of excellent sound absorption material.

1. Introduction

Polymer nanoporous structures serve as a highly versatile platform for a broad range of applications in widely different areas such as photonic structures, microfluid channels (nanofluidics), catalysis, sensors, medicine, and pharmacy and drug delivery. These great potential applications have received much attention recently. The electrospun nanoporous materials offer the potential for direct fabrication of biologically based, high-surface-area porous materials without the use of multiple synthetic steps, or postprocessing surface treatments [1–5].

Pore structure and connectivity determine how electrospun nanoporous materials perform in applications such as adsorption, separation, filtering, catalysis, fluid storage and transport. Depending on the particular area of applications the required properties of the nanoporous materials have to be optimized by controlling the size and distribution of porosity. How to control nanoporous size and porosity distribution is the forefront topic in nanotechnology [6–9].

In this paper, we suggested a general strategy for the synthesis of microspheres with nanoporosity by electrospinning, experimental results and theoretical models are presented to explain how to prepare electrospun nanoporous materials. The numbers and sizes of the pores could be controlled by tunable voltage or flow rate applied in the electrospinning process. With the increase of voltage and the decrease of flow rate, ever-increasing numbers and ever-decreasing sizes of the nanoporous microspheres have appeared, and electrospun nanoporous materials will become a kind of excellent sound absorption material with optimization design.

2. Electrospinning-dilation

During the electrospinning process, a steady state flow of an infinite viscous jet pulled from a capillary orifice and accelerated by a constant external electric field is considered.

* Corresponding author.
E-mail addresses: xlanmail@21cn.com, lanxu@suda.edu.cn (L. Xu).

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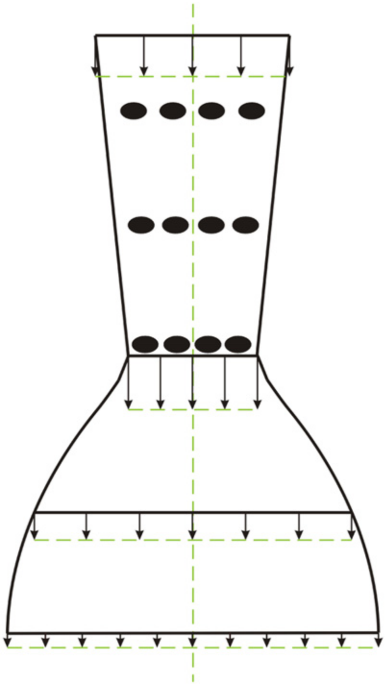

Fig. 1. Macromolecular chains are compacted during the electrospinning.

Theoretical model for electrospinning-dilation

Conservation of mass gives

$$\pi r^2 \rho u = Q, \tag{1}$$

where Q is the volume flow rate, ρ is the liquid density, u is the velocity, r is radius of the jet, the radius of the jet decreases with the increase of the velocity of the incompressible charged jet.

When the electrospinning velocity reaches a maximum in a very short time before it becomes unstable, macromolecules of the polymers are compacted together tighter and tighter during the electrospinning process as illustrated in Fig. 1. There must exist a critical minimal radius r_{cr} for all electrospun jet $r \le r_{cr}$ for continuous ultrafine fibers, and the critical maximal velocity is

$$u_{cr} = Q/\pi \rho r_{cr}^2. \tag{2}$$

However, the velocity can exceed this critical value u_{cr} if a higher voltage is applied. In cases when the radius of the jet reaches the value of the critical value $r = r_{cr}$, and the jet speed exceeds its critical value $u > u_{cr}$, in order to keep the conservation of mass equation, the jet dilates by decreasing its density, leading to porosity of the electrospun fibers, we call this phenomenon electrospinning-dilation.

Theoretical analysis of experimental results

PBS solutions with the additive 'Yunnan Baiyo' and mixed solvent of CHCL3(CF) and isopropyl alcohol were electrospun under different voltages and flowrates. Fig. 2 shows an SEM image of electrospun nanoporous microspheres.

Case 1

The flow rate was 1.5 ml/h, and the applied voltages connected to the needle varied from 8 to 15 KV. Fig. 3 shows the effect of applied voltage on the diameter of the electrospun nanoporous microspheres. It can be seen that with the increase of voltage, ever-decreasing sizes of the electrospun micro spheres with nanoporosity have appeared.

This phenomenon can be also explained by the following equation:

$$\pi r_{cr}^2 \tilde{\rho} u_0 = \pi R^2 \tilde{\rho} u_{\min} = Q, \tag{3}$$

where $\tilde{\rho}$ is the density of dilated microsphere, u_0 is the velocity of the charged jet at $r = r_{cr}$, R is the maximal radius of the microsphere, $u_{\min}$ is the minimal velocity. Higher voltage means higher value of the jet speed (u_0) at $r = r_{cr}$, and a more drastic electrospinning-dilation process happens, resulting in a lower density ($\tilde{\rho}$) of dilated microsphere, smaller size (R) of the microsphere and smaller pores as well.

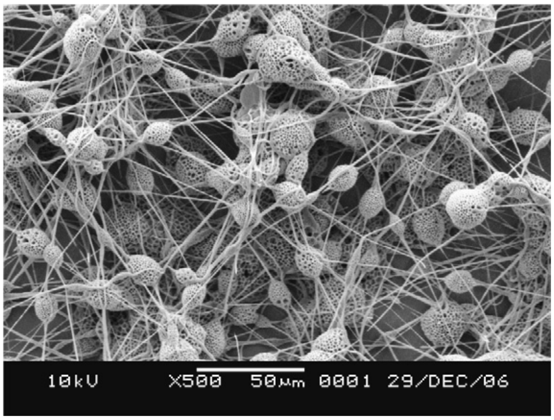

Fig. 2. SEM image of electrospun nanoporous microspheres.

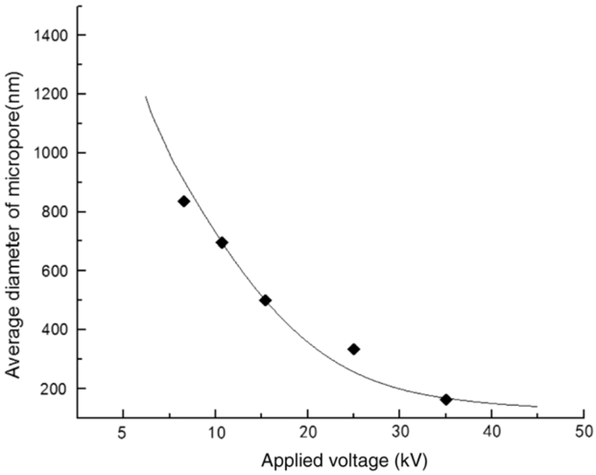

Fig. 3. Effect of applied voltage on the diameter of the electrospun nanoporous microspheres.

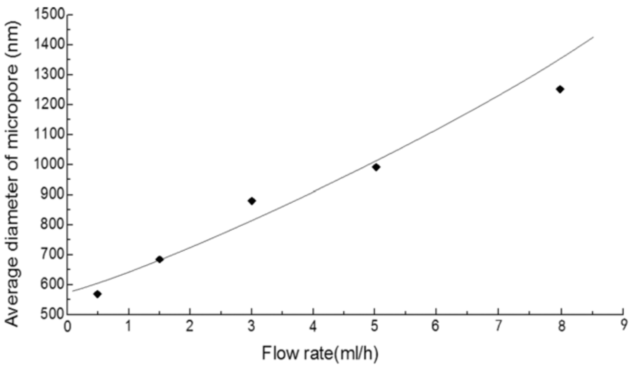

Fig. 4. Effect of flow rate on the diameter of the electrospun nanoporous microspheres.

Case 2

The applied voltage was 10 KV and the flow rate varied from 1.5 to 8 ml/h. Fig. 4 shows the effect of flow rate on the diameter of the electrospun nanoporous microspheres. It could be seen there that ever-increasing sizes of the electrospun nanoporous microspheres with the increase of flow rate appeared.

According to Eq. (2), the higher the flow rate, the higher the critical speed. That means electrospinning-dilation happens easily when the flow rate is relatively low.

In conclusion we found the porous sizes having uniform but tunable diameters can be controlled by voltage applied or flow rate in the electrospinning process.

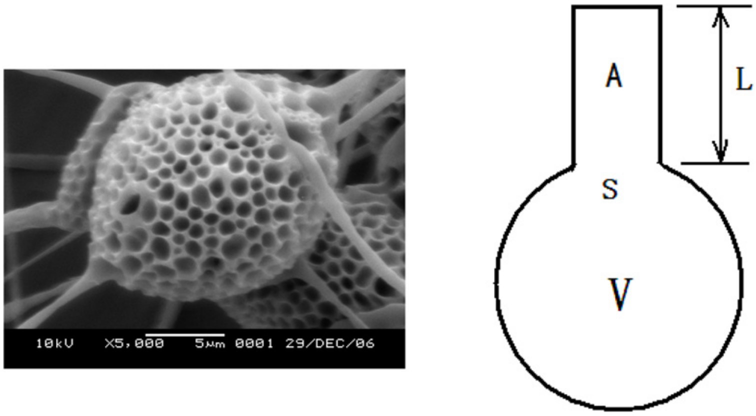

Fig. 5. Helmholtz resonator with extended neck.

3. Theoretical model for sound absorption materials

One of the most promising applications of micro-spheres with nano-porosity is sound absorption. These porous sound absorption materials contain a great amount of holes and exhaust the sound energy when sound waves travel through the inside reflecting and refracting. These micro-spheres with nano-porosity can be regarded as thousands of Helmholtz resonators forming together resonating with the sound of low frequency and absorbing its energy with a much wider band of sound frequency at the same time, see Fig. 5. Therefore, electrospun nanoporous materials will become a kind of excellent sound absorption material with optimization design.

The Helmholtz resonator is an effective acoustic attenuation device at low frequencies with its resonance dictated by the combination of cavity and neck and their relative orientation. The classical lumped analysis of this attenuator gives the resonance frequency as [10]

$$f_r = \frac{c_0}{2\pi}\sqrt{\frac{S_n}{V_c(L_n+\delta_n)}}, \tag{4}$$

where c_0 is the speed of sound, S_n is the neck's cross-sectional area, V_c is the resonator volume, L_n is the neck's length, and δ_n is the end correction to account for higher modes excited at the discontinuities, which can be determined by the geometry and location of the neck relative to the volume and main duct.

The acoustic impedance of a Helmholtz resonator which allows the evaluation of resonance frequency is calculated by [10]

$$Z_H = \frac{p_A}{\rho_0 c_0 u_p} = A_0^+ + A_0^-, \tag{5}$$

where p_A is the acoustic pressure at the neck outlet, ρ_0 is the density of air, u_p is the acoustic velocity magnitude at the neck outlet, and A_0^+ and A_0^- are the modal amplitudes corresponding to components traveling in the positive and negative directions in the neck.

Electrospun nanoporous materials can be regarded as the broadband resonance sound absorption structure of low frequency, which is comprised a lot from Helmholtz resonators with an extended neck. Then the acoustic impedance of these nanoporous materials might be written as follows

$$Z = \frac{1}{\frac{1}{Z_{H_1}} + \frac{1}{Z_{H_2}} + \frac{1}{Z_{H_3}} + \cdots + \frac{1}{Z_{H_i}}}, \tag{6}$$

where Z_{H_i} is the acoustic impedance of the ith Helmholtz resonator, $i = 1, 2, \ldots, n$.

4. Conclusions

A general strategy for the synthesis of microspheres with nanoporosity by electrospinning is presented. The results obtained by applying the theoretical models are in good agreement with the experimental data. The results show the flexibility and adaptation provided by the method have made the method a strong candidate for producing nanoporous materials. Electrospun nanoporous materials which can be regarded as thousands of Helmholtz resonators with an extended neck forming together will become a kind of excellent sound absorption material with optimized design.

Acknowledgments

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References

[1] X. Zhao, B. Xiao, A.J. Fletcher, et al., Hysteretic adsorption and desorption of hydrogen by nanoporous metal–organic frameworks, Science 306 (2004) 1012–1015.
[2] B. Wolfrum, Y. Mourzina, F. Sommerhage, A. Offenhäusser, Suspended nanoporous membranes as interfaces for neuronal biohybrid systems, Nano Lett. 6 (2006) 453–457.
[3] J.H. He, Y. Liu, L. Xu, et al., Micro sphere with nanoporosity by electrospinning, Chaos Solitons Fractals 32 (2007) 1096–1100.
[4] J.H. He, L. Xu, Y. Wu, et al., Mathematical models for continuous electrospun nanofibers and electrospun nanoporous microspheres, Polym. Int. 56 (11) (2007) 1323–1329.
[5] L. Xu, Y. Wu, Y. Liu, Electrospun nanoporous materials: reality, potential and challenges, Mater. Sci. Technol. 26 (11) (2010) 1304–1308.
[6] L. Xu, Y. Wu, Y. Nawaz, Numerical study of magnetic electrospinning processes, Comput. Math. Appl. 61 (8) (2011) 2116–2119.
[7] E. Harel, J. Granwehr, J.A. Seeley, et al., Multiphase imaging of gas flow in a nanoporous material using remote-detection NMR, Nature Mater. 5 (4) (2006) 321–327.
[8] A.K. Alomari, A new analytic solution for fractional chaotic dynamical systems using the differential transform method, Comput. Math. Appl. 61 (9) (2011) 2528–2534.
[9] Y. Aksoy, M. Pakdemirli, New perturbation–iteration solutions for Bratu-type equations, Comput. Math. Appl. 59 (8) (2010) 2802–2808.
[10] A. Selamet, I. Lee, Helmholtz resonator with extended neck, J. Acoustical Soc. Am. 113 (2003) 1975–1985.